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Direct observation of cavitation fields at 23 and 515 kHz [‡]

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Abstract

Direct observation of cavitation fields using photography, sonoluminescence and luminol “mapping” is reported for a 23 kHz horn sonicator and a 515 kHz plate transducer system. The effect of sound intensity and added surfactant on the cavitation fields is described. The observations support previously reported results suggesting significant differences in the cavitation fields between the two sonication systems.

Key words: sonoluminescence, cavitation, bubble coalescence, frequency

[‡] Part of this work was presented at the 11th meeting of the European Sonochemistry Society meeting at La Grande Motte, France, June 2008

Introduction

Over recent years, ultrasound has become a highly useful method for performing a wide range of chemical reactions and processes including chemical synthesis, materials production and water treatment [1 – 3]. Most of the effects arise from cavitation [4, 5]. One of the factors limiting the wider adoption of sonochemistry and sonoprocessing on a larger, industrial is the difficulty in predicting both the occurrence and consequences of cavitation and the effect of various experimental parameters on individual cavitation bubbles and bubble fields..

Among the parameters that affect cavitation, the effect of the ultrasound frequency is perhaps the least well understood. Frequency effects are influenced by both the number of bubble collapses per unit time and the product of each bubble collapse. Maximum bubble sizes are larger at lower frequencies and more reactive intermediates may be formed in each bubble collapse. A number of studies of the frequency effect have been published, some with conflicting results. However, most have generally followed the observations of Henglein [6] who reported that for a range of solutes in water, solvolysis (*i.e.* pyrolysis) was the main pathway at 1 MHz but that radical production and mechanical effects predominate at 20 kHz. Theron and co-workers [7] observed in the degradation of phenyltrifluoromethylketone in water at 30 kHz and 500 kHz a similar difference in mechanism. Several other reports have appeared of different products attributed to an alternative mechanism operating at different frequencies. [8 – 10]. Okitsu and co-workers [11] also showed that the frequency used influenced the size and shape of sonochemically synthesised gold nanoparticles.

In an attempt to clarify these effects, Price et al. [12-14] have used a number of methods to investigate cavitation bubbles and their products when produced using a 20 kHz horn sonicator or a 515 kHz plate transducer system. On the basis of different chemical products of sonolysis reactions and differences in acoustic emission and sonoluminescence quenching during sonication, they concluded that there were significant differences in the types of cavitation produced by a 515 kHz plate transducer system and a 20 kHz horn system of the type widely used for sonochemistry. At 515 kHz, stable cavitation was mainly observed where a bubble undergoes many oscillations during its lifetime. This can lead to significant amounts of solute adsorbing to the bubble interface and evaporating into the bubble so that a major reaction at this frequency is from pyrolysis of solutes. At lower frequencies

using horn type sonicators, transient cavitation is the predominant effect. Here, bubbles undergo few oscillations before finally collapsing so limiting the amount of solute entering the bubble. Since bubbles grow to a larger size and collapse more violently, larger quantities of free radicals can be produced by sonolysis and mechanical effects and attack by radical transfer into solution are the major mechanisms. Both transient and stable cavitation occur under each set of conditions but it is the balance between them that is dependent on the conditions used.

A number of studies have identified different cavitation bubble distributions arising from different types of ultrasound generators and configurations [15-18]. For example, as illustrated by Suslick et al. [15] a 20 kHz horn system usually gives strong cavitation in a limited zone near the horn tip while Petrier and co-workers [16, 17] used the emission from luminol to show that higher frequency emitters tend to give a more diffuse, widely distributed zone of cavitation. In this work, we report direct observation of cavitation bubbles at the two frequencies using video and sonoluminescence methods to provide confirmatory evidence for the previously reported effects as well as reporting how the ultrasound intensity and added surfactants change the cavitation bubble field.

Experimental

Sonication at 23 kHz was carried out with a Sonics & Materials VC 600 fitted with a 1 cm diameter titanium horn. 150 cm³ of the solution under investigation was measured into a beaker fitted with a water jacket to allow for temperature regulation. All the results reported were recorded at 20 ± 4 °C. The tip of the horn was positioned 1.5 cm below the surface of the solution; care was taken to ensure the horn and camera were placed in the same position for all experiments. A fresh sample of solution was used for each experiment when changing intensity. For higher frequency, 515 kHz sonication, an Undatim UL03/1 reactor employing a 5 cm diameter plate transducer was used. 150 cm³ of solution was contained in a jacketed cylinder over the transducer. The intensity of ultrasound used was measured by calibrated calorimetry in the usual manner [19].

High resolution video images were obtained using a Sony DCR106 video camera. In order to record sonoluminescence images, the apparatus was contained in a light-proof box. After saturation of the solution with Argon gas, images were recorded

on an Artemis CCD camera with a 35 mm focal length lens capable of an f2.8 aperture and incorporating a Sony ICX285AL lowlight CCD sensor. The camera has an imaging resolution of 1392 x 1040 pixels (1.4 megapixels). The total intensity of the emission was calculated after subtraction of background levels using ImageJ software [20] which was also used for further image manipulation. Unless indicated below, images were collected for 60 s sonication. For some experiments, enhanced images were obtained by sonicating a solution of chemiluminescent luminol. This was prepared by dissolving 1 mmol of luminol (3-aminophthalhydrazide, 97%), 0.1 mol hydrogen peroxide and 0.1 mol EDTA (ethylenediaminetetraacetic acid) in 1 dm³ of 0.1 M sodium carbonate. The solution was adjusted to pH 12 by adding sodium hydroxide.

All chemicals were obtained from Aldrich (UK). Aqueous solutions were prepared in deionised water from a MilliQ system and had a resistance > 10 MΩ.

Results and Discussion

In order to visualise the cavitation field under the different sonication conditions, initial experiments recorded the chemiluminescent emission from luminol solutions. Luminol “mapping” relies on emission from luminol that has captured a hydroxyl radical produced by sonolysis of water during cavitation collapse. It thus gives a good indication of where chemically active cavitation bubbles occur in a system. Figure 1 shows the results for a 23 kHz horn system. As expected, the cavitation activity is largely concentrated in a ‘cone’ just under the horn. As the intensity increases, the field of activity gets larger indicating a larger population of active bubbles.

The corresponding results for the 515 kHz system are shown in Figure 2. The differences from the horn system are clear. The cavitation field is much larger and more diffuse. It is layered indicating that there is a standing wave field; the spacing between the bright layers corresponds to the wavelength of sound in water at this frequency. This is consistent with previous observations that mainly stable cavitation is produced in this type of system since it would predominate in a standing wave field.

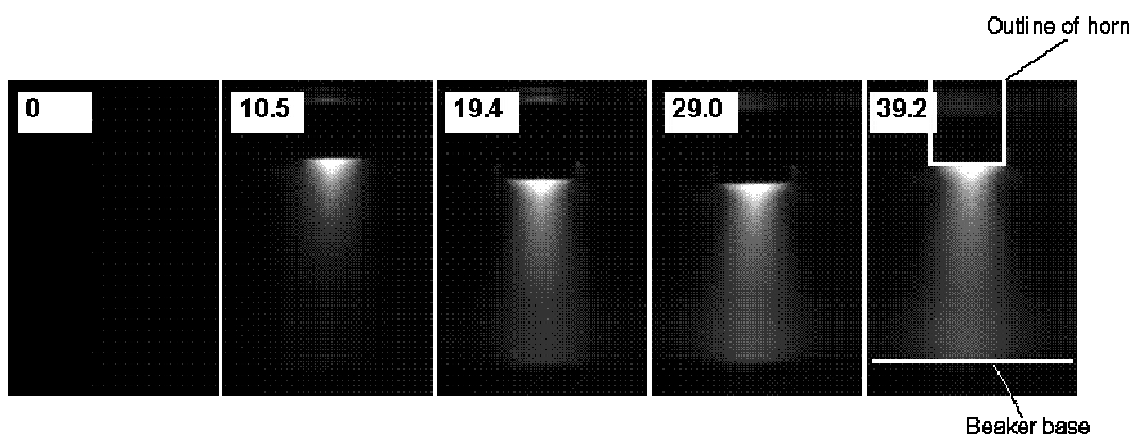


Figure 1. CCD images for luminol solutions sonicated at the indicated intensities (W cm^{-2}) using a 23 kHz horn. The position of the horn and the container are indicated on the right-hand image.

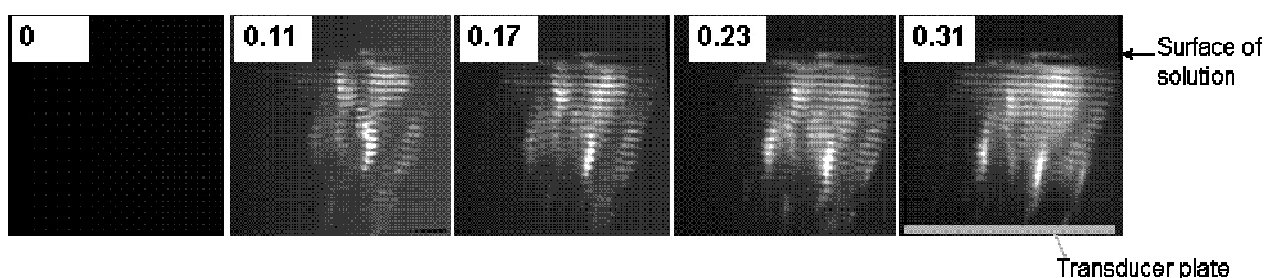


Figure 2. CCD images for luminol solutions sonicated at the indicated intensities (W cm^{-2}) using the 515 kHz plate transducer. The position of the transducer is indicated on the right-hand image.

Although not as apparent as in the 23 kHz horn system, the amount of light emission – and hence cavitation - increases with the ultrasound intensity. This can be seen in Figure 3 which plots the total emission integrated over the exposure time. Note that the luminescence is plotted on the same scale but the sound intensities are very different. This is partly a consequence of the larger emitted area of the 515 kHz plate but shows that higher cavitation activity as measured by hydroxyl radical production is produced at the higher frequency. The sound energy emitted corresponded to 1.2 – 6.0 W compared with 12 – 60 W into the same volume of solution with the 23 kHz horn.

The light emission patterns recorded in Figures 1 and 2 arise from secondary reactions with the products of cavitation collapse. To further investigate the

occurrence of cavitation and to eliminate any effect due to the trapping efficiency of the luminol or the lifetime of the luminol excited state or to other reactions, images of true sonoluminescence (SL) from argon-saturated pure water were recorded and are shown in Figure 4. These measurements are at the limit of our CCD camera and longer exposure times (5 min) were needed to obtain satisfactory images. They are similar in form to those from the luminol solutions and showed a similar increase of emission with rising intensity. The difference in the nature of the sound field between the two systems is thus confirmed. However, it is noticeable that the volume of solution from which emission occurs at 20 kHz in Figure 1 is larger than that in Figure 4(a) indicating that chemical effects (in this case reaction with sonolytically generated radicals) occurs around bubbles that are not necessarily sonoluminescent. This in part arises from the lifetime of the luminol excited state but also suggests that chemical effects occur in and around bubbles that do not reach the very high temperatures needed for sonoluminescence.

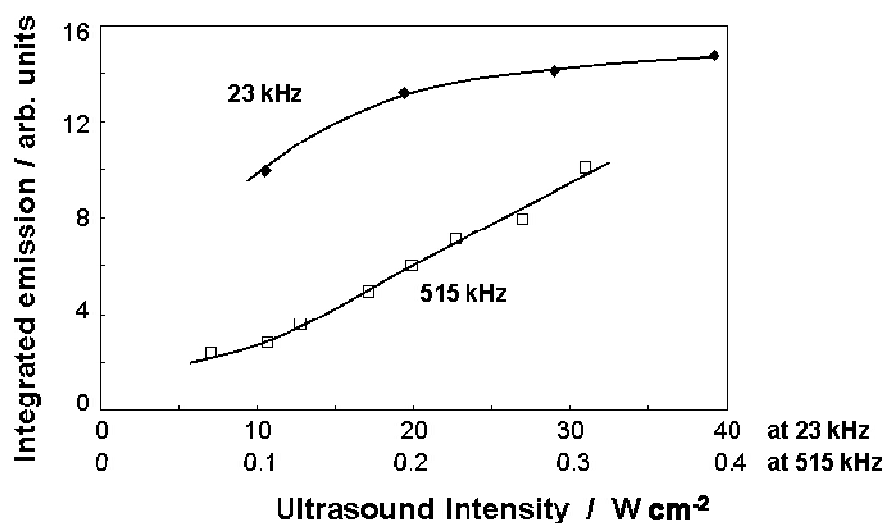


Figure 3. The effect of ultrasound intensity on the total integrated sonochemiluminescence emission from sonicated luminol solutions.

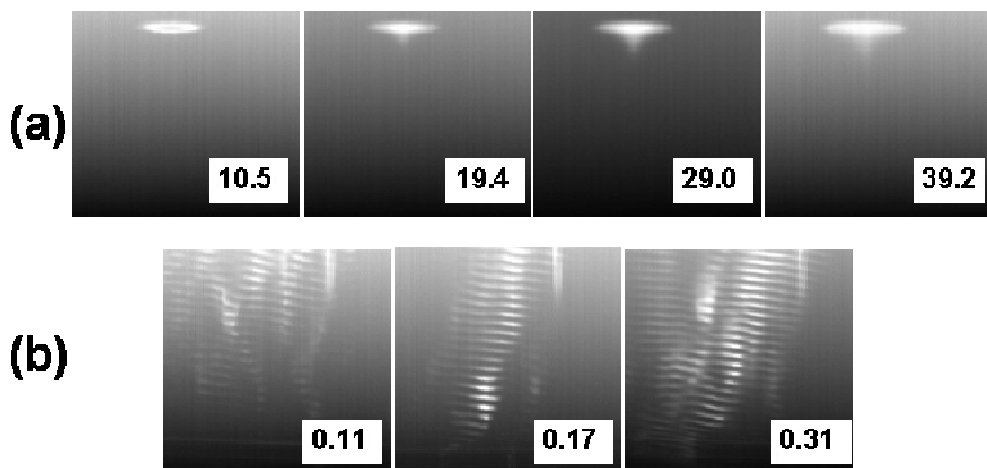


Figure 4. Sonoluminescence from sonicated water at the indicated intensities (Wcm^{-2}) (a) 23 kHz Horn, (b) 515 kHz plate transducer

Previous work looking at the effects of additives such as surfactants on SL and acoustic emission led Ashokkumar et al. [14, 21] to suggest that, in a stable cavitation field, the number of active bubbles is largely influenced by adsorption at the bubble-solution interface preventing bubble coalescence. Figure 5 shows the effect of adding the surfactant sodium dodecyl sulfate (SDS) on the SL emission at 515 kHz. The emission intensity is plotted as a function of SDS concentration in Figure 6. There is a significant increase in emission from solutions with low concentrations of SDS before it returns to levels similar to that from water at higher concentrations. The standing wave nature of this cavitation field is still readily apparent. In contrast, with the 20 kHz horn, there was little discernable effect on the field of bubbles. The ‘plume’ of activity emanating from the horn appeared somewhat larger at higher SDS concentrations although the total measured emission, also shown in Figure 6, remained fairly constant and fell at high concentrations. Previous observations of this type [14] have been attributed to electrostatic repulsion between small, SL (and sonochemically) active bubbles preventing their coalescence into larger, inactive bubbles. This effect is lessened when using a 23 kHz horn since the sound field produces much greater turbulence and bubble motion so that small changes in inter-bubble repulsions have much smaller influence. Interestingly, when the emission from luminol solutions was investigated as a function of added SDS, a significant decrease in emission was observed for both sonication systems. We interpret this as SDS

adsorbed at the bubble-solution interface trapping some of the hydroxyl radicals produced inside the bubble so that they cannot react with luminol in solution.

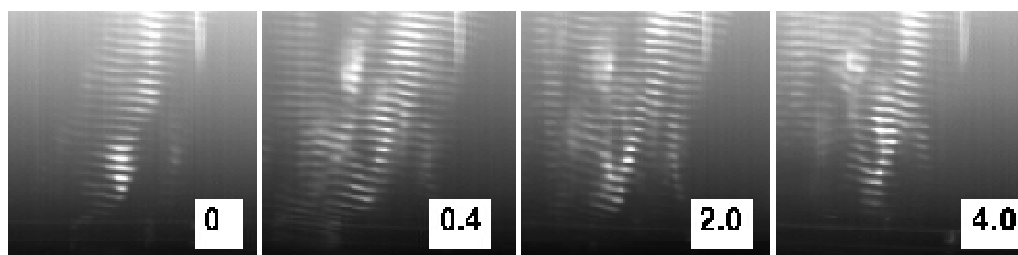


Figure 5. SL images of SDS solutions with the indicated concentrations (mM) sonicated with a 515 kHz plate transducer at 0.31 W cm^{-2}

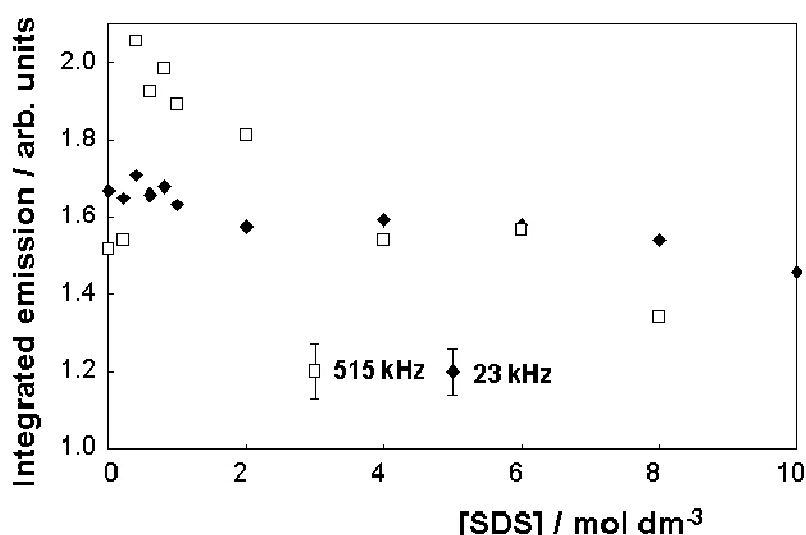


Figure 6. Effect of SDS concentration on the SL emission intensity during sonication (23 kHz Horn at 29 W cm^{-2} , 515 kHz at 0.31 W cm^{-2})

This bubble coalescence can in fact be observed visually in the sonicated solutions. Figure 7 shows photographs taken from a video of the system being sonicated. In pure water (Figure 7(a)) a range of bubble sizes can be observed. These are not individual cavitation bubbles but are gas bubbles which arise from coalescing bubbles. This is demonstrated by their behaviour when the sound field is switched off when the bubbles remain intact for some 30 – 60 s during which time they drift to the surface of the solution. On switching the sound field back on, large bubbles immediately reappear. In contrast, these larger bubbles are not visible during

sonication of 1 mmol dm^{-3} solution of SDS (Figure 7(b)). The electrostatic repulsion between cavitation bubbles prevents their coalescence into the larger gas bubbles. Hence there are more active bubbles in the system so that greater SL emission is observed. The cloud of cavitation bubbles is just visible in the video although difficult to discern in the still photographs. In this case, switching off the sound results in the cavitation bubbles disappearing instantaneously. Significantly, addition of salt to this solution eliminates the surfactant effect and larger gas bubbles are again observed (Figure 7(c)). The system behaves in an identical manner to water since the salt screens and hence eliminates the electrostatic shielding of the surfactant.

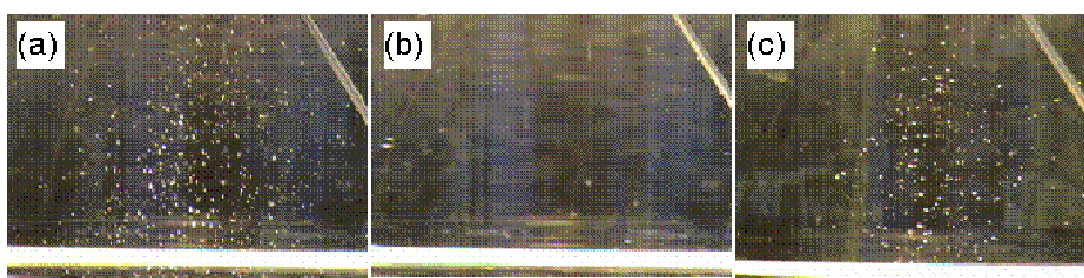


Figure 7. Photographs of 515 kHz sonication at 0.31 W cm^{-2} . (a) pure water (b) aqueous 1 mM SDS solution (c) aqueous 1 mM SDS + 0.1 M sodium perchlorate

Conclusions

The optical and SL photographs presented here confirm previously reported results that the cavitation fields produced by a 515 kHz plate transducer and a 23 kHz horn sonicator are significantly different. The higher frequency apparatus produces a standing wave field. This further emphasises that when comparing results in the literature, not only the frequency of ultrasound used but also the type of apparatus used must be considered. It is known that standing wave fields can be generated at low frequencies around 20 kHz [22 - 25] and the nature of cavitation under these conditions is currently being investigated.

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